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(54) **Liquid compositions for refrigeration systems containing fatty amines, fatty amides, and reaction products of fatty acylating agents.**

(57) This invention relates to a liquid composition comprising (A) at least one fluorine-containing hydrocarbon containing 1 to 3 carbon atoms, (B) an efficiency improving or wear reducing amount of an additive selected from the group consisting of at least one fatty amine, at least one fatty amide, at least one reaction product of at least one fatty carboxylic acylating agent and at least one amine selected from the group consisting of a polyamine, a hydroxy amine and a mixture thereof, and at least one mixture thereof, and (C) an effective amount of a lubricant selected from the group consisting of at least one carboxylic ester, at least one polyalkylene glycol, at least one polycarbonate, and at least one mixture thereof. The liquid compositions containing the fatty amine, the fatty amide, the reaction product of a fatty carboxylic acylating agent have improved efficiency and antiwear properties. These compositions provide effective protection against wear, especially aluminum on steel wear. The compositions help prevent formation of metal debris during compressor operations.

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This invention relates to liquid compositions which are useful in refrigerator systems, especially those which use environmentally friendly fluorine containing hydrocarbon. The liquid compositions contain a fatty amine, a fatty amide, and/or a reaction product of a fatty carboxylic acylating agent and a polyamine of hydroxyamine together with a carboxylic ester, polyoxyalkylene glycol, or polycarbonate lubricant.

5 The discovery that CFCs contribute substantially to degradation of the ozone layer lead to an urgent search for suitable, ozone-friendly replacements. Several candidate refrigerant fluids have since been identified. Many of these fall into the category of hydrofluorocarbons, or HFCs. Hydrofluorocarbons contain at least one carbon atom, and have at least one C-F bond and at least one C-H bond.

10 Another category of possible CFC replacements is hydrochlorofluorocarbons, or HCFCs. These are similar to HFCs, with the important distinction that HCFCs also contain at least one chlorine atom. Hydrochlorofluorocarbons, while not completely free of adverse effects on the ozone layer, represent a substantial improvement over CFCs in this respect, and may in many cases represent at least an interim solution to the problem of CFC replacement.

15 However, the drive to replace CFCs in refrigeration systems did not end with the development of HFCs. Refrigeration systems use a mixture of refrigerant fluid with lubricant, due to the need to provide internal lubrication to the compressor parts. Therefore, the new generation of HFC refrigerant fluids had to be matched to a suitable category of compatible - i.e., miscible - lubricants. There was relatively little difficulty finding lubricants for use with CFCs, due to the strong solubilizing influence of the chlorine atoms. However, the presence of the C-H bond in HFCs greatly reduces their miscibility. Thus, it was soon realized that the hydrocarbon lubricants customarily used with CFCs were not miscible with HFCs.

20 Compatible lubricants, such as specific esters and polyalkylene glycols, have been found. However, there remains a need for additives which may be combined with these compatible lubricants. Additives are needed to provide wear protection to the compressor, particularly in compressors using CFC refrigerants because of the absence of chlorine. A particular problem in compressor lubrication is aluminum on steel wear. For example, high silica content aluminum, such as aluminum 390, may act to cause wear on soft steel. When wear is high, the color of the lubricant becomes dark as metal debris is present in the lubricant. This metal debris reflects damage to the aluminum or steel parts of the compressor. It is desirable to provide additives to reduce wear.

25 A need also exists to improve the efficiency of compressor operation by reducing the energy needed to run the compressor. Efficiency is generally measured by use of a compressor calorimeter system that measures the amount of power required to operate a given compressor such that a given volume of air (or other gas) is maintained within a given temperature range over a given amount of time; the results may be expressed in terms of BtUs of cold generated per watt of electricity consumed. Efficiency may be improved, for example, by use of an additive which provides improved friction properties, and therefore reduces energy requirements of compressors is desired.

30 EP 461,262 (Idemitsu Kosan Co.) relates to a refrigerator composition for hydrofluorocarbon refrigerants. The composition includes a polyoxyalkylene glycol and/or a specified polyester compound together with (a) a partial fatty acid ester of a polyhydric alcohol and (b) a phosphate compound and/or a phosphite compound.

WO 92/010130 (Henkle Corporation) relates to a lubricant for refrigerant heat transfer fluids. The lubricants are specific esters and specific mixtures of esters of polyhydric alcohol.

40 U. S. Patent 4,744,316 (Magid et al.) relates to refrigeration lubricants. The lubricants are polyoxyalkylene glycols. The lubricant may include other additives, such as oxidation resistance and thermal stability improvers, corrosion inhibitors, metal deactivators, lubricity additives, viscosity index improvers, pour and/or floc point depressants, detergents, dispersants, antifoaming agents, anti-wear agents, and extreme pressure resistant additives.

45 According to one aspect of the present invention there is provided a liquid composition comprising (A) at least one fluorine-containing hydrocarbon containing 1 to 3 carbon atoms, (B) an efficiency improving or wear reducing amount of an additive selected from the group consisting of at least one fatty amine, at least one fatty amide, at least one reaction product of at least one fatty carboxylic acylating agent and at least one amine selected from the group consisting of a polyamine, a hydroxy amine and a mixture thereof, and at least one mixture thereof, and (C) an effective amount of a lubricant selected from the group consisting of at least one carboxylic ester, at least one polyalkylene glycol, at least one polycarbonate, and at least one mixture thereof.

50 The liquid compositions containing the fatty amine, the fatty amide, the reaction product of a fatty carboxylic acylating agent have improved efficiency and antiwear properties. These compositions provide effective protection against wear, especially aluminum on steel wear. The compositions help prevent formation of metal debris during compressor operations.

55 Various preferred features and embodiments of the present invention will now be described by way of non-limiting example.

In the specification and claims, unless the context indicates otherwise, the use of the term hydrocarbyl

or alkyl group is meant to encompass all isomeric arrangements of the groups. The arrangements include primary, secondary, and tertiary, as well as iso and neo-arrangements of the group.

In the specification and claims, the use of the term alkylene is meant to encompass divalent hydrocarbon groups. For instance, propylene is a divalent hydrocarbon group having 3 carbon atoms.

5 Throughout this specification and claims, all parts and percentages are by weight, temperatures are in degrees Celsius, and pressures are at or near atmospheric unless otherwise clearly indicated.

The term "polyoxyalkylene" refers to groups containing more than one ether linkage and terminating in a hydroxy, hydrocarbyl, amino, or amido group.

10 The term "hydrocarbyl" includes hydrocarbon, as well as substantially hydrocarbon, groups. Substantially hydrocarbon describes groups which contain non-hydrocarbon substituents which do not alter the predominantly hydrocarbon nature of the group. Non-hydrocarbon substituents include halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, amido, sulfoxy, etc., groups. The hydrocarbyl group may also have a heteroatom, such as sulfur, oxygen, or nitrogen, in a ring or chain. In general, no more than about 2, preferably no more than one, non-hydrocarbon substituents will be present for every ten carbon atoms in the hydrocarbyl group. Typically, there will be no such non-hydrocarbon substituents in the hydrocarbyl group. Therefore, the hydrocarbyl group is purely hydrocarbon.

15 The term "lower" as used herein is intended to describe such groups which contain a total of up to 7 carbon atoms. For example, lower alkyl groups include methyl, ethyl, propyl, butyl, pentyl, and hexyl groups.

#### 20 Fluorine-Containing Hydrocarbon (A)

The fluorine-containing hydrocarbon present in the liquid compositions contains at least one C-H bond as well as C-F bonds. In addition to these two essential types of bonds, the hydrocarbon also may contain other carbon-halogen bonds such as C-Cl bonds. Because the liquid compositions of the present invention are primarily intended for use as refrigerants, the fluorine-containing hydrocarbon preferably contains from one to about three, preferably one to two, carbon atoms.

In one preferred embodiment, the hydrocarbon contains only carbon, hydrogen, and fluorine. The hydrocarbons containing chlorine as well as fluorine and hydrogen are referred to as hydrochlorofluorocarbons or HCFCs. Examples of hydrochlorofluorocarbons include HCFC-22 (difluorochloromethane); HCFC-123 (1,1-dichloro-2,2,2-trifluoroethane); and HCFC-141b (1,1-dichloro-1-fluoroethane).

30 The compounds containing only carbon, hydrogen, and fluorine are referred to herein as hydrofluorocarbons or HFCs. In general, fluorine-containing hydrocarbons which are useful as refrigerants are fluoromethanes and fluoroethanes boiling at a relatively low temperature at atmospheric pressure, e.g., below 30°C. Specific examples of the fluorine-containing hydrocarbons useful in the liquid compositions of the present invention include HFC-125 (pentafluoroethane); HFC-134a (1,1,1,2-tetrafluoroethane); HFC-32 (trifluoromethane); HFC-143a (1,1,1-trifluoroethane); and, HFC-152a (1,1-difluoroethane).

The fluorine containing hydrocarbon also includes blends of fluorine containing hydrocarbons. Examples of these blends include HFC-32 and HFC-125 (60%:40%); HFC-32 and HFC-134a (30%:70%); HFC-125 and HFC-143a (45%:55%); HFC-32, HFC-125, and HFC-134a (30%:10%:60%); and HFC-125, HFC-143a, and HFC-134a (44%:52%:4%), wherein all percentages are weight percentages.

40 The amount of fluorine-containing hydrocarbon is the level typically used for the refrigeration system. The amount of fluorine containing hydrocarbon used in the refrigerator systems are generally specified by the manufacturer of the refrigeration system. Thus, the liquid compositions of the present invention may generally contain from about 10%, or from about 20% up to about 90%, or up to about 85% of the fluorine-containing hydrocarbon. In one embodiment, the fluorine-containing hydrocarbon is present in an amount from about 45%, or from about 50%, or from about 55 % up to about 90%, or up to about 80%, or up to about 75% by weight of the liquid composition. More generally, the liquid compositions will comprise from about 50% up to about 99% by weight of the fluorine-containing hydrocarbon. In another embodiment, the liquid compositions contain from about 70% up to about 99% by weight of the fluorine-containing hydrocarbon. When the fluorine-containing hydrocarbon is used at levels greater than 50% by weight of the lubricant, then the liquid compositions are generally suited for use as automotive and commercial and industrial refrigeration systems.

50 In one embodiment, the fluorine-containing hydrocarbon is present in an amount from about 10%, or from about 25%, or from about 30% up to about 55%, or up to about 50%, or up to about 45% by weight of the lubricant. When the fluorine-containing hydrocarbon is present in an amount less than about 45%, then the liquid compositions are generally suited for household refrigeration systems.

Fatty Amine, Fatty Amide, or Reaction Product of a Fatty Acylating Agent (B)

In addition to the fluorine-containing hydrocarbon (A), the liquid composition contains a fatty amine, a fatty amide, a reaction product of a fatty carboxylic acylating agent and a polyamine or a hydroxyamine, or mixtures thereof (B). Generally, (B) is present in an amount from about 0.01%, or from about 0.1%, or from about 0.3%, up to about 3%, or up to about 2%, or up to about 1.5% by weight of the lubricant. Generally, the fatty amine and/or fatty amide independently have at least one hydrocarbyl group containing from about 8 to about 30, preferably from about 10 to about 22, more preferably from about 12 to about 18, carbon atoms. Examples of these hydrocarbyl groups include octyl, decyl, decenyl, dodecyl, dodecenyl, tridecyl, tetradecyl, hydroxytetradecyl, hexadecyl, hydroxyhexadecyl, octadecyl, oleyl, coco, soya, and tallow groups.

The fatty amine may be any fatty amine which is compatible in the liquid compositions of the present invention. The fatty amine may be a mono- or polyamine. The fatty amine may also be a hydroxyalkyl, polyoxyalkylene, or ether fatty amine.

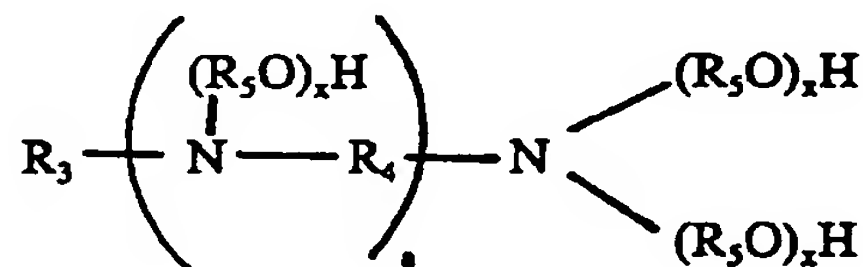
In one embodiment, the fatty amine may be represented by the formula:



wherein  $R_1$  is a hydrocarbyl group containing from about 8 to about 30 carbon atoms, and each  $R_2$  is independently hydrogen, an alkyl group containing from one to about 20 carbon atoms, a hydroxyalkyl group, or a polyoxyalkylene group. Generally,  $R_1$  may contain about 10 to about 22, preferably from about 12 to about 18, carbon atoms. Examples of  $R_1$  include octyl, decyl, decenyl, dodecyl, dodecenyl, tridecyl, tetradecyl, hydroxytetradecyl, hexadecyl, hydroxyhexadecyl, octadecyl, oleyl, coco, soya, and tallow groups.

Preferably, each  $R_2$  is independently hydrogen; or, an alkyl group having from one to about eight carbon atoms, such as a methyl, ethyl, propyl or butyl group; a hydroxyalkyl group containing from about two to about six, preferably two to about four, more preferably about two carbon atoms, such as hydroxyethyl and hydroxypropyl groups; and a polyoxyalkylene group having from about one to about 25, more preferably from one to about 15, more preferably from one to about ten carbon atoms. In one embodiment, the polyoxyalkylene group contains from about one to about five oxyalkylene groups. The alkylene groups of the polyoxyalkylene groups contain from about two to about six, preferably from about two to about four carbon atoms. Examples of alkylene groups include ethylene, propylene, and butylene groups.

In another embodiment, the fatty amine is represented by the formula:



wherein  $R_3$  is a hydrocarbyl group containing from about 8 to about 30 carbon atoms,  $R_4$  and  $R_5$  are each independently an alkylene group,  $a$  is zero or one, and each  $x$  is independently a number from zero to about 25. In one embodiment, at least one of  $x$  is at least one.

Preferably,  $R_3$  is a hydrocarbyl group containing from about 10 to about 22, more preferably about 12 to about 18 carbon atoms.  $R_3$  is preferably an alkyl group. In one embodiment,  $R_3$  is defined the same as  $R_1$ .

Preferably, each  $x$  is independently a number from one to about 25, preferably one to about 15, more preferably one to about ten. In one embodiment, each  $x$  is independently a number from one to about five. In another embodiment, each  $x$  is one.

Each  $R_5$  and  $R_4$  is independently an alkylene having from about two to about eighteen, preferably from about two to about six, more preferably from about two to about four, carbon atoms. The alkylene groups include ethylene, propylene, and butylene groups.

The above fatty amine may be prepared by techniques well known in the art, and many such fatty amines are commercially available. The primary amines may be single amines or mixtures of amines such as those derived from fatty acids obtained by the hydrolysis of fatty oils such as tallow oils, sperm oils, coconut oils, etc. Specific examples of fatty amines include saturated, as well as unsaturated, aliphatic amines. Examples



of fatty amines include laurylamine, tridecylamine, tetradecylamine, hexadecylamine, stearyl amine, oleylamine, cocoamine, soyamine, and tallow amine. Examples of commercially available primary amines are "Armeen" primary amines (products available from Akzo Chemical). These Armeen primary amines are available in both distilled and technical grades. Also suitable are mixed fatty amines such as Akzo's Armeen-C (co-

amine), Armeen-O (oleylamine), Armeen-OL, Armeen-T (tallow amine), Armeen-HT (hydrogenated tallow amine), Armeen S (soyamine) and Armeen SD (distilled soyamine).  
In one embodiment, the fatty amine is a hydroxyalkyl fatty amine. They may be prepared, for example, by reaction of an amine, such as those described herein, containing at least 8 carbon atoms, with various amounts of alkylene oxides such as ethylene oxide, propylene oxide, etc. The hydroxyalkyl fatty amines may be prepared by reacting an amine with a fatty epoxide. The amine may be any simple amine such as lower alkyl amines, which include methyl, ethyl, or butyl amines. The epoxide is generally an aliphatic epoxide having at least 8, preferably about 10, more preferably about 12, up to about 24, preferably 20 carbon atoms. Examples of useful aliphatic epoxides include heptyl oxide, octyl oxide, stearyl oxide, oleyl oxide, and the like. Mixtures of epoxides may also be used, for instance commercial mixtures of epoxides having from 14 to about 16 carbon atoms and

14 to about 18 carbon atoms.  
Generally, the hydroxyalkyl group contains from about two to about eighteen, preferably two to about six, more preferably from about two to about four carbon atoms. Hydroxyalkyl groups include hydroxyethyl and hydroxypropyl groups. In another embodiment, the fatty amine is a dihydroxyalkyl fatty amine. Examples of fatty amines include 2-hydroxyethyl dodecylamine, 2-hydroxyethyl tetradecylamine, 2-hydroxypropyl pentadecylamine, 2-hydroxyethyl oleylamine, 2-hydroxyethyl soyamine, (2-hydroxyhexadecyl) ethylamine, bis(2-hydroxyhexadecyl) hydroxyethylamine, bis-(2-hydroxyethyl) octadecylamine, bis(2-hydroxyethyl) oleylamine, and mixtures thereof. Also included are 2-hydroxyethoxyethyl oleylamine, and bis(2-hydroxyethoxyethyl) tallowamine.

A number of useful fatty amines where a in the above formula is zero are available from the Akzo Chemical, under the general trade designation "Ethomeen" and "Propomeen". Specific examples of such products include "Ethomeen C/15", which is an ethylene oxide condensate of a cocoamine containing about 5 moles of ethylene oxide; "Ethomeen C/20" and "C/25", which also are ethylene oxide condensation products from cocoamine containing about 10 and 15 moles of ethylene oxide, respectively; "Ethomeen O/12", which is an ethylene oxide condensation product of oleylamine containing about 2 moles of ethylene oxide per mole of amine; "Ethomeen S/15" and "S/20", which are ethylene oxide condensation products with soyamine containing about 5 and 10 moles of ethylene oxide per mole of amine, respectively; and "Ethomeen T/12, T/15" and "T/25", which are ethylene oxide condensation products of tallowamine containing about 2, 5 and 15 moles of ethylene oxide per mole of amine, respectively. "Propomeen O/12" is the condensation product of one mole of oleyl amine with 2 moles propylene oxide.

Commercially available examples of alkoxyated amines where a in the above formula is one include Ethoduomeen T/13 and T/20 which are ethylene oxide condensation products of N-tallow trimethylene diamine containing 3 and 10 moles of ethylene oxide per mole of diamine, respectively.

The fatty polyamine diamines include mono- or dialkyl, symmetrical or asymmetrical ethylene diamines, propane diamines (1,2, or 1,3), and polyamine analogs of the above. Suitable commercial fatty polyamines are Duomeen C (N-coco-1,3-diaminopropane), Duomeen S (N-soya-1,3-diaminopropane), Duomeen T (N-tallow-1,3-diaminopropane), and Duomeen O (N-oleyl-1,3-diaminopropane). "Duomeens" are commercially available from Akzo Chemical.

In another embodiment, the fatty amine is an ether amine. The ether amine may be represented by the formula



wherein  $R^*_1$  is a hydrocarbyl group having from about 8 to about 30 carbon atoms,  $R^*_2$  is a divalent alkylene, usually alkylene, group having from 2 to about 6 carbon atoms, and x is a number greater than zero. In another embodiment,  $R^*_1$  is defined the same as  $R_1$ . In another embodiment,  $R^*_2$  is defined the same as  $R_5$ . Generally, x is a number from 1 to about 30. In one embodiment, x equals one.

Commercially available ether amines are SURFAM® amines, produced and marketed by Mars Chemical Company, Atlanta, Georgia. Preferred ether amines are exemplified by those identified as SURFAM® P14B (decyloxypropylamine), SURFAM® P16A (linear  $C_{18}$ ), and SURFAM® P17B (tri-decyloxypropylamine). The carbon chain lengths of the SURFAM® amines described above and used hereinafter are approximate and include the oxygen ether linkage. For example, a  $C_{14}$  SURFAM® amine would have the following general formula:  $C_{10}H_{21}OC_3H_8NH_2$ .

In another embodiment, the fatty amine or alkylphenyl is prepared by reacting one of the above described fatty amines with an aldehyde and nitropropane. The alkyl substituent on the alkylphenyl may contain up to about 12 carbon atoms, preferably about 4 to 12, most typically 7 or 8. The aldehyde generally has from one to about eight, preferably from one to about four carbon atoms. Examples of aldehydes include formaldehyde

and formaldehyde precursors. Formaldehyde precursors include materials which under reaction conditions react like formaldehyde. Examples of formaldehyde precursors are paraformaldehyde and trioxane.

In another embodiment, the fatty amine is obtained from a dimer or trimer acid. The acid is converted to an amide, dehydrated, and then hydrogenated as is known to those in the art. Dimer and trimer acids are prepared by dimerization of unsaturated fatty acids. Generally, the dimer acids have an average of from about 18, preferably from about 28 to about 44, preferably to about 40, carbon atoms. In one embodiment, the dimer acids have preferably about 36 carbon atoms. The dimer acids are preferably prepared from C<sub>18</sub> fatty acids, such as oleic acids.

In another embodiment, (B) is a fatty amide. Fatty amides may be derived from fatty acids. Examples of fatty amides include octyl, decyl, decenyl, dodecyl, dodecenyl, tridecyl, tetradecyl, hydroxytetradecyl, hexadecyl, hydroxyhexadecyl, octadecyl, oleyl, coco, soya, and tallowamides. The fatty amide may be represented by the formula



wherein R<sub>6</sub> is a hydrocarbyl group containing from about 8 to about 30 carbon atoms, and each R<sub>7</sub> is independently hydrogen, an hydrocarbyl group containing from one to about twenty carbon atoms, a hydroxyalkyl group, or a polyoxyalkylene group. R<sub>6</sub> and R<sub>7</sub> are defined the same as R<sub>1</sub> and R<sub>2</sub>, respectively.

In another embodiment, the fatty amide may be represented by the formula



wherein R<sub>7</sub> is a hydrocarbyl group containing from about 8 to about 30 carbon atoms, R<sub>8</sub> are each independently an alkylene group, and each y is independently a number from zero to about 25. In one embodiment, at least one of y is at least one. Preferably, R<sub>7</sub>, R<sub>8</sub>, and y are defined the same as R<sub>3</sub>, R<sub>5</sub>, and x, respectively.

In one embodiment, the fatty amide is a hydroxyalkyl fatty amide or a polyoxyalkylene fatty amide. These materials are prepared by reacting a fatty amide with one of the above described alkylene oxides. A polyoxyalkylene fatty amide may also be referred to as a polyoxyalkylated fatty amide. Preferably the fatty amide is polyoxypropylated or polyoxyethylated, more preferably polyoxyethylated fatty amide. Examples of fatty amides which may be polyoxyalkylated include oleylamide, stearylamine, tallowamide, soyamide, cocoamide, and laurylamide. Polyoxyalkylated fatty amides are available commercially from Akzo Company, under the trade name Ethomid®, and Lonza, Inc., under the tradename Unamide™. Specific examples of these polyoxyalkylated fatty amides include Ethomid® HT/15 and HT/60, which are hydrogenated tallow amides treated with 5 and 50 moles of ethylene oxide respectively; Ethomid® O/15, which is an oleic amide treated with 5 moles of ethylene oxide; Unamide™ C-2 and C-5, which are cocoamides treated with 2 and 5 moles of ethylene oxide, respectively; and Unamide™ L-2 and L-5, which are lauramides treated with 2 and 5 moles of ethylene oxide, respectively.

The liquid compositions of the present invention also may include a reaction product of a fatty carboxylic acylating agent and at least one polyamine or a hydroxyamine. The reaction products of the fatty carboxylic acylating agent and the polyamine are generally imidazolines of the fatty carboxylic acylating agent. The reaction products of the fatty carboxylic acylating agent is generally an oxazoline of the fatty carboxylic acylating agents.

The fatty carboxylic acylating agents generally have from about 8 to about 30 carbon atoms. The fatty groups of the acylating agent are the same as those defined for the fatty amine and/or amide above. Carboxylic acids include the polycarboxylic acids or carboxylic acids or anhydrides having from 2 to about 4 carbonyl groups, preferably 2. The polycarboxylic acids include succinic acids and anhydrides and Diels-Alder reaction products of unsaturated monocarboxylic acids with unsaturated carboxylic acids (such as acrylic, methacrylic, maleic, fumaric, crotonic and itaconic acids). Preferably, the fatty carboxylic acids include octanoic, oleic, stearic, linoleic, dodecanoic, and tall oil acids, preferably stearic acid.

In one embodiment, the fatty carboxylic acylating agent is reacted with at least one polyamine. The polyamines may be aliphatic, cycloaliphatic, heterocyclic or aromatic. Examples of the polyamines include alkylene

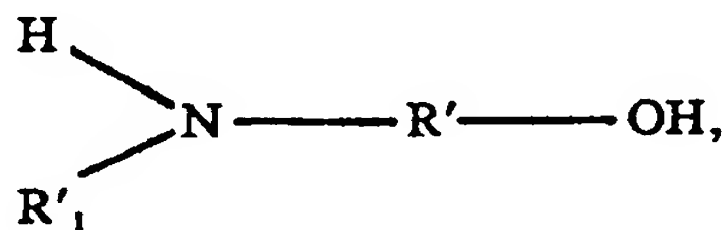
polyamines and heterocyclic polyamines. Useful polyamines are described in U.S. Patent 4,234,435 at Col. 21, line 4 to Col. 27, line 50, these passages being incorporated herein by reference for its disclosure of polyamines and heterocyclic polyamines.

A preferred reaction product of a carboxylic acid and polyamine is made by reacting an alkylene polyamine with a mixture of fatty acids having from 5 to about 30 mole percent straight chain acid and about 70 to 95% mole branch chain fatty acids. Among the commercially available mixtures are those known widely in the trade as isostearic acid. These mixtures are produced as a by-product from the dimerization of unsaturated fatty acids as described in U.S. Patents 2,812,342; and 3,260,671. These patents are hereby incorporated by reference for their disclosure of these reaction products and methods of making the same.

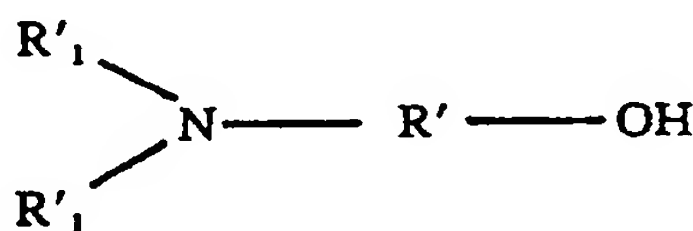
The branched chain fatty acids can also include those in which the branch is not alkyl in nature, such as found in phenyl and cyclohexyl stearic acid and the chloro-stearic acids. Branched chain fatty carboxylic acid/alkylene polyamine reaction products have been described extensively in the art. See, for example, U.S. Patents 3,110,673; 3,251,853; 3,326,801; 3,337,459; 3,405,064; 3,429,674; 3,468,639; and 3,857,791. These patents are hereby incorporated by reference for their disclosures of fatty acid/ polyamine condensates for their use in lubricating oil formulations.

In another embodiment, the reaction product of a fatty carboxylic acid and a polyamine are further reacted with one or more of the epoxides described herein. The reaction product of a fatty acid, polyamine and epoxide is described in U.S. Patent 3,240,575 which is hereby incorporated by reference for its teachings to carboxylic acids, polyamines, epoxides and reaction products and methods of making the reaction products. Examples of useful carboxylic acid- polyamine reaction products include the reaction of commercial diethylene triamine with isostearic acid, commercial tetraethylene pentamine and isostearic acid, and an alkylene amine mixture consisting of triethylene tetramine and diethylene triamine in weight ratio of 3:1 reacted with a mixture a naphthenic acid and oleic acid.

In another embodiment, the fatty carboxylic acylating agent is reacted with a hydroxyamine. Hydroxyamines are also referred to as alkanolamines. Typically, the hydroxyamines are primary, secondary or tertiary alkanolamines or mixtures thereof. Such amines can be represented by the formulae:

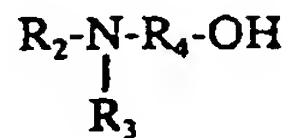


and



wherein each  $\text{R}'_1$  is independently a hydrocarbyl group of one to about eight carbon atoms or hydroxyhydrocarbyl group of one to about eight carbon atoms, or to about four, and  $\text{R}'$  is a divalent hydrocarbyl group of about two to about 18 carbon atoms, preferably two to about four. The group  $-\text{R}'-\text{OH}$  in such formulae represents a hydroxyhydrocarbyl group.  $\text{R}'$  can be an acyclic, alicyclic or aromatic group. Typically,  $\text{R}'$  is an acyclic straight or branched alkylene group such as an ethylene, 1,2-propylene, 1,2-butylene, 1,2-octadecylene, etc. group. Where two  $\text{R}'_1$  groups are present in the same molecule they can be joined by a direct carbon-to-carbon bond or through a heteroatom (e.g., oxygen, nitrogen or sulfur) to form a 5-, 6-, 7- or 8-member ring structure. Examples of such heterocyclic amines include N-(lower hydroxy alkyl)-morpholines, -thiomorpholines, -piperidines, -oxazolidines, -thiazolidines and the like. Typically, however, each  $\text{R}'_1$  is independently a methyl, ethyl, propyl, butyl, pentyl or hexyl group.

In one embodiment, the alkanolamines are represented by the formula



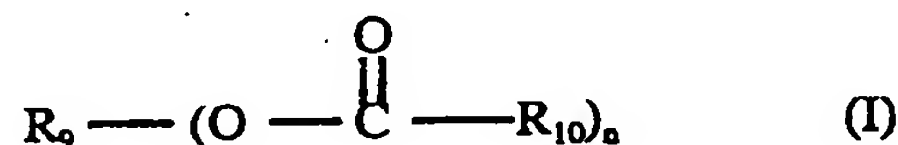
wherein  $R_2$  and  $R_3$  are each independently alkyl or hydroxyalkyl groups having from 1 to about 10, or to about 6, or to about 4 carbon atoms.  $R_4$  is preferably an alkylene group having from 1, or about 2 up to about 10 or to about 4 carbon atoms. In another embodiment,  $R_4$  contains 2 or 3 carbon atoms. In one embodiment,  $R_2$  and  $R_3$  are each independently a methyl, ethyl, propyl or butyl group.

Examples of these hydroxyamines include mono-, di- and triethanolamine; diethyl ethanolamine; di(3-hydroxypropyl)amine, N-(3-hydroxybutyl) amine, N-(4-hydroxybutyl)amine, N,N-di(2-hydroxypropyl) amine, N-(2-hydroxyethyl) morpholine and its thioanalog, N-(2-hydroxyethyl)cyclohexyl amine, N-(3-hydroxycyclopentyl) amine, ortho-, meta-, and para-aminophenol, N-(hydroxyethyl) piperazine, N,N'-di(hydroxyethyl)piperazine, and the like. Preferred amines are dimethylethanolamine and diethylethanolamine.

The hydroxyamine is reacted with the fatty carboxylic acylating agent at a temperature sufficient to remove water and form cyclic reaction products. The temperature is typically from about 100°C to about 200°C.

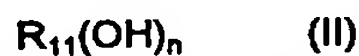
#### Lubricant (C)

The liquid compositions also contain a carboxylic ester lubricant, a polyoxyalkylene glycol lubricant, a polycarbonate lubricant, or a mixture thereof. The carboxylic ester is prepared by reacting a carboxylic acylating agents with a polyhydroxy compound containing at least two hydroxy groups. The carboxylic esters may be represented by the general formula



wherein  $R_9$  is a hydrocarbyl group, each  $R_{10}$  is independently hydrogen, a straight chain lower hydrocarbyl group, a branched chain hydrocarbyl group, or a straight chain hydrocarbyl group containing from about 8 to about 22 carbon atoms, provided that at least one  $R_{10}$  group is hydrogen, a lower straight chain hydrocarbyl or a branched chain hydrocarbyl group, or a carboxylic acid- or carboxylic ester-containing hydrocarbyl group, and  $n$  is at least 2.

The polyhydroxy compounds used to make the carboxylic esters may be represented by the general formula

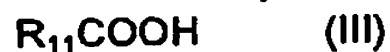


wherein  $R_{11}$  is a hydrocarbyl group and  $n$  is at least 2. The hydrocarbyl group may contain from 4 to about 20 or more carbon atoms, and the hydrocarbyl group may also contain one or more nitrogen and/or oxygen atoms. The polyhydroxy compounds generally will contain from about 2 to about 10 hydroxy groups, and preferably from about 2 to about 6 hydroxyl groups. The polyhydroxy compound may contain one or more oxyalkylene groups, and, thus, the polyhydroxy compounds include compounds such as polyetherpolyols.

Specific examples of polyhydroxy compounds useful in the present invention include ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, glycerol, neopentyl glycol, 1,2-, 1,3- and 1,4-butanediols, pentaerythritol, dipentaerythritol, tripentaerythritol, triglycerol, trimethylolpropane, sorbitol, hexaglycerol, 2,2,4-trimethyl-1,3-pentanediol, etc. Mixtures of any of the above polyhydroxy compounds may also be utilized.

The polyhydroxy compounds used in the preparation of the carboxylic esters (I) also may contain one or more nitrogen atoms. For example, the polyhydroxy compound may be an alkanol amine containing from 3 to 6 hydroxy groups. In one preferred embodiment, the polyhydroxy compound is an alkanol amine containing at least two hydroxy groups, and more preferably at least three hydroxy groups.

The carboxylic acylating agents utilized in the preparation of the carboxylic esters useful in the liquid compositions of the present invention may be characterized by the following general formula



wherein  $R_{11}$  is (a), hydrogen, (b) a straight chain lower hydrocarbyl group, (c) a branched chain hydrocarbyl group, or (d) a mixture of one or both of (b) and (c) with a straight chain hydrocarbyl group containing from about 8 to about 22 carbon atoms, or (e) a carboxylic acid- or carboxylic acid ester-containing hydrocarbyl group. Stated otherwise, at least one  $R_{10}$  group in the ester of Formula I must contain a lower straight chain hydrocarbyl group or a branched chain hydrocarbyl group. The straight chain lower hydrocarbyl group ( $R_{11}$ )



contains from 1 to about 7 carbon atoms, and in a preferred embodiment, contains from 1 to about 5 carbon atoms. The branched chain hydrocarbyl group may contain any number of carbon atoms and will generally contain from 4 to about 20 carbon atoms. In one preferred embodiment, the branched chain hydrocarbon group contains from 5 to 20 carbon atoms and in a more preferred embodiment, contains from about 5 to about 14 carbon atoms. The higher molecular weight straight chain hydrocarbyl group containing from 8 to about 22 carbon atoms will contain, in some embodiments, from 8 to about 18 carbon atoms, and in more preferred embodiments from 8 to about 14 carbon atoms.

In one preferred embodiment, the branched chain hydrocarbyl groups are characterized by the structure

$$-C(R_{12})(R_{13})(R_{14})$$

wherein  $R_{12}$ ,  $R_{13}$  and  $R_{14}$  are each independently alkyl groups, and at least one of the alkyl groups contains two or more carbon atoms. Such branched chain alkyl groups, when attached to a carboxyl group, are referred to in the industry as neo groups, and the acylating agents are referred to as neo acylating agents. In one embodiment,  $R_{12}$  and  $R_{13}$  are methyl groups and  $R_{14}$  is an alkyl group containing two or more carbon atoms.

Any of the above hydrocarbyl groups ( $R_{11}$ ) may contain one or more carboxy groups or carboxy ester groups such as  $-COOR_{15}$ , wherein  $R_{15}$  is a lower alkyl, hydroxyalkyl, or hydroxy alkyl group. In one embodiment, the hydrocarbyl group contains from two to about six, preferably from two to about four, carboxy groups. Such substituted hydrocarbyl groups are present, for example, when the carboxylic acylating agent  $R_{11}COOH$  (III) is a dicarboxylic acylating agent or a monoester of a dicarboxylic acylating agent. Generally, however, the acylating agent  $R_{11}COOH$  (III) is a monocarboxylic acylating agent. Mixtures of monocarboxylic acylating agents and minor amounts of dicarboxylic acylating agents or anhydrides are useful in preparing the carboxylic esters (I).

Examples of carboxylic acylating agents containing a straight chain lower hydrocarbyl group include formic acid, acetic acid, propionic acid, butyric acid, pentanoic acid, hexanoic acid, and heptanoic acid. Examples of carboxylic acylating agents wherein the hydrocarbyl group is a branched chain hydrocarbyl group include 2-ethyl butyric acid, 2-hexadecanoic acid, isostearic acid, 2-methylhexanoic acid, 3,5,5-trimethylhexanoic acid, 2-ethylhexanoic acid, neoheptanoic acid, neodecanoic acid, and commercial mixtures of branched chain carboxylic acids such as the mixture identified as Neo 1214 acid from Exxon.

The third type of carboxylic acylating agents which can be utilized in the preparation of the carboxylic esters are the acylating agents containing a straight chain hydrocarbyl group containing from 8 to about 22 carbon atoms. As noted previously, these higher molecular weight straight chain acylating agents can be utilized only in combination with one of the other acylating agents described above since the higher molecular weight straight chain acylating agents are not soluble in the fluorohydrocarbons. Examples of such higher molecular weight straight chain acylating agents include decanoic acid, dodecanoic acid, stearic acid, lauric acid, behenic acid, etc. Examples of dicarboxylic acylating agents include maleic acid, succinic acid, adipic acid, oxalic acid, pimelic acid, glutaric acid, suberic acid, azelaic acid, sebacic acid, etc.

In another embodiment, the carboxylic acylating agents utilized to prepare the carboxylic esters may comprise a mixture of a major amount of monocarboxylic acylating agent and a minor amount of dicarboxylic acylating agent. The presence of the dicarboxylic acylating agents results in the formation of esters of higher viscosity. An example of such a mixture of 80 parts of neoheptanoic acid and 20 parts of succinic acid.

In one embodiment, the carboxylic ester is the reaction product of (I) a neo hydroxy compound and (II) one or more carboxylic acylating agents. The neo hydroxy compounds are reacted with (a) a monocarboxylic acylating agent having four or five carbon atoms, (b) a monocarboxylic acylating agent having from about 7 to about 15 carbon atoms, or a mixture thereof. The monocarboxylic acylating agent (a) may be isobutyric, valeric, 2-methylbutyric, or neopentanoic acid or anhydride. Isopentanoic acid, commercially available from Union Carbide, is a mixture of valeric acid and 2-methylbutanoic acid with an approximate weight ratio of (66:34). In another embodiment, the monocarboxylic acylating agent may be neo pentanoic acid, available from Exxon Chemical Company.

The monocarboxylic acylating agent (b) generally contains from about 7, or about 8 up to about 15, or to about 12, or to about 10 carbon atoms. The monocarboxylic acylating agents (b) may be linear or branched, and include "iso" and "neo" branched acylating agents. Examples of these acylating agents include n-octanoic acid, neoheptanoic acid, neodecanoic acid, 2,2,4-trimethylpentanoic acid, 2-hexadecanoic acid, isostearic acid, 2-methylhexanoic acid, 3,5,5-trimethylhexanoic acid, 2-ethylhexanoic acid, 2,2,4-trimethylpentanoic acid, isononanoic acid, isoheptanoic acid, isodecanoic acid, neoheptanoic acid, neodecanoic acid, and ISO Acids and NEO Acids available from Exxon Chemical Company, Houston, Texas USA. ISO Acids are isomer mixtures of branched acids and include commercial mixtures such as ISO Heptanoic Acid, ISO Octanoic Acid, and ISO Nonanoic Acid, as well as developmental products such as ISO Decanoic Acids and ISO 810 Acid. Of the ISO Acids, ISO Octanoic acid and ISO Nonanoic acid are preferred. Neo acids include commercially available mixtures such as NEO Pentanoic Acid, NEO Heptanoic Acid, and NEO Decanoic Acid, as well as

developmental products such as ECR-909 (NEO C<sub>9</sub>) Acid, and ECR-903 (NEO C<sub>1214</sub>) Acid and commercial mixtures of branched chain carboxylic acids such as the mixture identified as NEO 1214 acid from Exxon.

In one embodiment, the carboxylic esters are prepared from a mixture of monocarboxylic acylating agent having four or five carbon atoms (a) and monocarboxylic acylating agent having from about 7 to about 15 carbon atoms (b). When forming these carboxylic esters greater than 55%, or greater than 57%, or greater than 59% of the ester groups are derived from the monocarboxylic acylating agent (a).

In another embodiment, the carboxylic esters are prepared from the above combination, except provided that greater than 55%, or greater than 57%, or greater than 59% of the ester groups are derived from (b).

In another embodiment, the carboxylic ester is at least one carboxylic ester of a polycarboxylic acylating agent, preferably a dicarboxylic acylating agent and a polyhydroxy compound, or a mixture of monocarboxylic and polycarboxylic acylating agent, preferably dicarboxylic acylating agents and a polyhydroxy compound. The presence of the dicarboxylic acylating agents results in the formation of esters of higher viscosity. The complex esters are formed by having a substantial portion of the dicarboxylic acylating agents reacted with more than one polyol. The reaction is generally coupling of polyols through the dicarboxylic acylating agent or anhydride. Examples of mixtures of mono- and dicarboxylic acylating agents include succinic anhydride and 3,5,5-trimethylhexanoic acid; azelaic acid and 2,2,4-trimethylpentanoic acid; adipic acid and 3,5,5-trimethylhexanoic acid; sebacic acid and isobutyric acid; adipic acid and a mixture of 50 parts 3,5,5-trimethylhexanoic acid and 50 parts neoheptanoic acid; and neoheptanoic acid and a mixture of 50 parts adipic acid and 50 parts sebacic acid. The use of mixtures containing larger amounts of dicarboxylic acylating agents should be avoided since the product ester will contain larger amounts of polymeric esters, and such mixtures may be insoluble in the fluorohydrocarbons. An example of such a mixture is 80 parts of neoheptanoic acid and 20 parts of succinic acid. Viscosity and average molecular weight of the ester can be increased by increasing the amount of dicarboxylic acylating agent and decreasing the amount of monocarboxylic acylating agent.

In one embodiment, the esters are made by reacting a polyol with a mixture of a dicarboxylic acylating agent and a monocarboxylic acylating agent. Preferably, one equivalent of polyol is reacted with from about 0.07, preferably from about 0.17 to about 0.33, preferably to about 0.23 equivalents of dicarboxylic acylating agent or anhydride and from about 0.67, preferably from about 0.77 to about 0.93, preferably to about 0.83 equivalents of monocarboxylic acylating agent.

The formation of esters by the reaction of carboxylic acylating agents with the polyhydroxy compounds described above can be effected by heating the acylating agents, the polyhydroxy compounds, with or without an esterification catalyst, which includes acid catalysts, to an elevated temperature while removing water or low molecular weight alcohols formed in the reaction. Generally, temperatures of from about 75°C to about 200°C or higher are sufficient for the reaction. The reaction is completed when water or low molecular weight alcohol is no longer formed, and such completion is indicated when water or low molecular weight esters can no longer be removed by distillation.

In some instances, it is desired to prepare carboxylic esters wherein not all of the hydroxyl groups have been esterified. Such partial esters can be prepared by the techniques described above and by utilizing amounts of the acylating agents which are insufficient to esterify all of the hydroxyl groups.

Examples of particularly useful carboxylic esters include (a) triesters of trimethylolpropane and n-pentanoic acid; (b) esters prepared by reacting n-pentanoic acid, iso-octanoic acid, and 3,5,5-trimethylhexanoic acid with monopentaerythritol, wherein the weight ratio of the acids is (15:30:55); (c) esters prepared from the acid of (b) and monopentaerythritol except the weight ratio of (5:10:85); and (d) esters prepared from the acids of (b) and dipentaerythritol except the ratio of the acids is (15:5:80). In one embodiment, the esters are prepared without a catalysts.

The following examples illustrate the preparation of various carboxylic esters which are useful as lubricants (B) in the liquid compositions of the invention.

#### Example 1

A mixture of 872 parts (6.05 moles) of 2-ethylhexanoic acid, 184 parts (2 moles) of glycerol and 200 parts of toluene is prepared and blown with nitrogen while heating the mixture to about 60°C. Para-toluene sulfonic acid (5 parts) is added to the mixture which is then heated to the reflux temperature. A water/toluene azeotrope distills at about 120°C. A temperature of 125-130°C is maintained for about 8 hours followed by a temperature of 140°C for 2 hours while removing water. The residue is the desired ester.

#### Example 2

A mixture of 536 parts (4 moles) of trimethylol propane and 680 parts (4 moles) of a commercial C<sub>810</sub>

straight chain methyl ester is prepared, and 5 parts of tetrapropyl orthotitanate are added. The mixture is heated to 200°C with nitrogen blowing. Methanol is distilled from the reaction mixture. When the distillation of methanol is completed by nitrogen blowing, the reaction temperature is lowered to 150°C, and 408 parts (4 moles) of acetic anhydride are added in a slow stream. A water azeotrope begins to evolve when 50 parts of toluene are added. When about 75 parts of a water/acetic acid mixture has been collected, the distillation ceases. Acetic acid (50 parts) is added and additional water/acetic acid mixture is collected. The acetic acid addition is repeated with heating until no water can be removed by distillation. The residue is filtered and the filtrate is the desired ester.

#### Example 3

A mixture of 408 parts (3 moles) of pentaerythritol and 660 parts (3 moles) of a commercial straight chain methyl ester comprising a mixture of about 75% C<sub>12</sub> methyl ester and about 25% C<sub>14</sub> methyl ester, (CE1270 from Procter & Gamble) is prepared with 5 parts of tetrapropyl orthotitanate, and the mixture is heated to 220°C under a nitrogen purge. No reaction occurs. The mixture then is cooled to 130°C, and 250 parts of acetic acid are added. A small amount of para-toluenesulfonic acid is added and the mixture is stirred at about 200°C for 2 days, and 60 parts of methanol are removed. At this time, 450 parts of acetic anhydride are added and the mixture is stirred at 150°C until the acetic acid/water azeotrope no longer evolves. The residue is filtered through a filter aid, and the filtrate is the desired ester of pentaerythritol.

#### Example 4

A mixture of 850 parts (6.25 moles) of pentaerythritol, 3250 parts (25 moles) of neoheptanoic acid, and 10 parts of tetrapropyl orthotitanate is prepared and heated to 170°C. Water is evolved and removed by distillation. When the evolution of water ceases, 50 parts of acidified clay are added and some additional water is evolved. A total of about 250 parts of water is removed during the reaction. The reaction mixture is cooled to room temperature and 310 parts of acetic anhydride are added to esterify the remaining hydroxyl groups. The desired ester is obtained.

#### Example 5

A mixture of 320 parts (1.26 moles) of dipentaerythritol, 975 parts (1.25 moles) of neoheptanoic acid and 25 parts of Amberlyst 15 catalyst is prepared and heated to 130°C. At this temperature water evolution is slow, but when the temperature is raised to 150°C, about 65% of the theory water is collected. The last amounts of water are removed by heating to 200°C. The product is a dark viscous liquid.

#### Example 6

A mixture of 1072 parts (8 moles) of trimethylolpropane, 2080 parts (16 moles) of neoheptanoic acid and 50 parts of Amberlyst 15 is prepared and heated to about 130°C. A water/acid azeotrope evolves and is removed. When about 250 of the azeotrope has been removed, 584 parts (4 moles) of adipic acid are added and the reaction continues to produce an additional 450 parts of distillate. At this time, 65 parts of trimethylolpropane are added to the mixture and additional water is removed. The residue is filtered and the filtrate is the desired ester.

#### Example 7

Esters are prepared by reacting mixtures of isononanoic acid (1) and adipic acid (2) with trimethylolpropane (3), in the presence of a tetrapropyl orthotitanate catalyst. The reactants are charged to a flask and heated until reaction ceases, as indicated by termination of water collection in a distillation trap, at which point the reaction mixture has reached about 220°C. A vacuum is applied to remove volatile components, and the flask contents are cooled and filtered to produce the liquid ester product.

Properties of the products are as follows:

5

Product	Moles			Catalyst, grams	Viscosity, cSt		Molecular Weight
	(1)	(2)	(3)		40°C	100°C	
A	44	2	16	13	76.6	9.1	611
B	40	4	16	12	116	12.3	694
C	16	2	6.7	5	141	13.9	723

10 As can be seen, increasing the fraction of dicarboxylic acid results in a higher viscosity, higher average molecular weight (as measured by vapor phase osmometry) ester material.

Example 8

15 The procedure of Example 7 is used to prepare esters from isononanoic acid (1), adipic acid (2) and neopentylglycol (3), giving the following product properties:

20

Product	Moles			Catalyst, grams	Viscosity,cSt		Molecular Weight
	(1)	(2)	(3)		40°C	100°C	
A	2	1	2	2	80	10.5	588
B	10.7	6.7	12	5	106	13.2	665
25 C	8.3	8.3	12.5	8	220	22.1	758

Example 9

30 The procedure of Example 7 is used to prepare esters from isononanoic acid (1), isooctanoic acid (2), isobutanoic acid (3), adipic acid (4) and pentaerythritol (5), giving the following product properties:

35

	Moles					Catalyst
Product	(1)	(2)	(3)	(4)	(5)	grams
A	7	7	7	1.5	6	5
B	7.2	7.2	6	1.8	6	5

40

Product	Viscosity, cSt		Molecular Weight
	40°C	100°C	
45 A	149.5	14.0	733
B	194	16.9	802

50 Example 10

The procedure of Example 7 is used to prepare the ester in Table 3.

55



TABLE 3

			<u>Moles</u>	
			Adipic Acid	ISO Nonanoic Acid (2)
5	<u>Example</u>	<u>TMP(1)</u>		
	10A	1	0.1	2.8
10	10B	1	0.125	2.75
	10C	1	0.25	2.45
	10D	1	0.30	2.4
15	10E	1	0.35	2.3
		<u>Viscosity</u>		
		@40°C	@100°C	
20	10A	69.4	8.65	
	10B	76.6	9.14	
25	10C	119	12.3	
	10D	140	14	
	10E	185	16.8	

(1) TMP - Trimethylol propane

(2) Available from Exxon Chemical Company

#### 35 Example 11

A reaction vessel is charged with 2010 parts (15 moles) of trimethylolpropane, 6534 parts (45 moles) of 2,2,4-trimethylpentanoic acid (available commercially from Exxon Corporation under the trade name ISO Octanoic acid), and 8 parts of methanesulfonic acid. The mixture is heated to 150°C and water is removed. The temperature is increased to 200°C and the temperature is maintained for eight hours. After water evolution, the reaction mixture is vacuum stripped to 200°C and 20 mm Hg. The residue is filtered and the filtrate is the desired product. The product has a neutralization acid number of 0.06 and a kinematic viscosity of 32 cSt at 40°C.

#### 45 Example 12

A reaction vessel is charged with 2814 parts (21 moles) of trimethylolpropane, 6854 parts (67 moles) of isopentanoic acid (available commercially from Union Carbide), which is a mixture of 66% by weight valeric acid and 34% by weight 2-methylbutyric acid), 5 parts methanesulfonic acid, 50 parts of an aromatic solvent. The reaction mixture is heated to 145°C over three hours. The reaction mixture is heated to 165°C over three hours. The temperature of the mixture is maintained for 13 hours. A total of 1100 milliliters of water is collected. The reaction mixture is vacuum stripped to 180-200°C and 10-15 mm Hg. The residue is filtered and the filtrate is the desired product. The product has a 0.009 acid number, and a kinematic viscosity of 10.2 cSt at 40°C and 2.65 cSt at 100°C.

#### 55 Example 13

An ester is prepared by the procedure of Example 12 using 372 parts (1 mole) of tripentaerythritol, 790

parts (5 moles) of 3,5,5-trimethylhexanoic acid, 204 parts (2 moles) of isopentanoic acid, 73 parts (0.5 mole) of adipic acid, and 4 parts of tetrapropyl orthotitanate.

#### Example 14

5

A reaction vessel is charged with 3082 (69 equivalents) of trimethylolpropane, 3312 (23 equivalents) of 2,2,4-trimethylpentanoic acid, 3634 (46 equivalents) of isobutyric anhydride and 10 parts (0.1 equivalent) of methanesulfonic acid. The reaction mixture is heated under nitrogen to 115°C. The temperature is maintained between 115°C to 150°C for 6 hours. The reaction temperature is maintained at 150°C for 10 hours while 798  
10 milliliters of distillate is collected. The mixture is heated to 200°C and held for 8 hours while 32 milliliters of distillate is collected. The total distillate collected is 860 milliliters. The mixture is cooled to 130°C where 350 parts (4.4 equivalents) of isobutyric anhydride are added to the reaction vessel. The mixture is stirred at 130°C for 24 hours. The reaction mixture is vacuum stripped at 8-10 mm Hg and 120-150°C for 8 hours. The acid number after the stripping was 4.2. The reaction mixture is stripped to 190°C and 8-10 mm Hg for 6 hours.  
15 The acid number after this stage of stripping is 0.84. The residue is vacuum stripped for 8 hours at 195°C and 10 mm Hg. The acid number after this stage of stripping is 0.051. The residue of the product has a kinematic viscosity of 14.0 centistokes at 40°C and 3.1 centistokes at 100°C. The acid number of the product is 0.05.

#### Example 15

20

A reaction vessel is charged with 2286 parts (9.0 moles) of dipentaerythritol, 1422 parts (9 moles) of isononanoic acid, 1836 parts (18 moles) of neopentanoic acid, and 8 parts of methanesulfonic acid. The reaction is heated to 140°C and the temperature is maintained for 18 hours. Water is collected (460 milliliters) by distillation. An additional charge of isononanoic acid (4266 parts, 27 moles) is added to the reaction vessel. The  
25 reaction is heated to 200°C and the temperature is maintained for 18 hours. The reaction is vacuum stripped to 200°C and 10 mm Hg. After 15 hours of stripping the acid number was 0.2. The residue was treated with alumina (800 parts) and the mixture is heated to 110°C and the temperature is maintained for 4 hours. The product is filtered and the filtrate is the desired product. The filtrate has a kinematic viscosity of 720 centistokes at 40°C and 30.5 centistokes (at 100°C).

30

#### Example 16

A reaction vessel is charged with 166 parts (1.22 moles) of pentaerythritol, 151 parts (0.4 moles) of tri-pentaerythritol, 439 parts (2.7 moles) of isononanoic acid, 391 parts (2.7 moles) of 2,2,4-trimethylpentanoic  
35 acid, 214 parts (1.35 moles) of isobutyric anhydride, and 4 parts of tetrapropyl orthotitanate. The reaction mixture is heated to 170°C and the temperature is maintained for 24 hours. Water is collected by distillation (130 milliliters). The reaction is vacuum stripped for 3 hours at 170°C and 1 mm Hg. The product is filtered and the residue has a kinematic viscosity of 133.8 centistokes (at 40°C) and 13.27 centistokes (at 100°C). The acid number of the product is 0.1.

40

#### Example 17

A reaction vessel is charged with 192 parts (1.41 moles) of pentaerythritol, 242 parts (0.95 moles) of di-pentaerythritol, 1337 parts (8.46 moles) of isononanoic acid, 406 parts (2.82 moles) of 2,2,4-trimethylpenta-  
45 noic acid, and 3 parts of tetrapropyl orthotitanate. The reaction mixture is heated to 210°C and the temperature is maintained for 30 hours while water is removed. The reaction mixture is vacuum stripped to 210°C and 10 mm Hg. The residue is treated with alumina and filtered. The filtrate is the desired product and has a kinematic viscosity of 171.7 centistokes (at 40°C) and 15.4 centistokes (at 100°C).

50

#### Example 18

A reaction vessel is charged with 374 parts (2.75 moles) of pentaerythritol, 465 parts (1.83 moles) of di-pentaerythritol, 3042 parts (19.25 moles) of isononanoic acid, 217 parts (1.37 moles) of isobutyric anhydride, and 4 parts of methanesulfonic acid. The reaction mixture is heated to 130°C and the temperature is maintained  
55 for 24 hours, while 360 milliliters of water is collected. An additional charge of isobutyric anhydride (20 grams) is added to the reaction mixture at 100°C. The reaction mixture is heated to 190°C and blown with nitrogen at 2 standard cubic feet per hour for 6 hours. The product is vacuum stripped for 24 hours at 200°C and 10 mm Hg. After 16 hours of vacuum stripping the acid number is 0.15. After 24 hours of vacuum stripping the acid

number is 0.1. The residue is treated with alumina (300 parts) at 120°C. The acid number after alumina treatment is 0.05. The mixture is filtered through a pad of alumina and diatomaceous earth. The filtrate is the desired product and has a kinematic viscosity of 182 centistokes (at 40°C) and 15.6 centistokes (at 100°C). The filtrate has a acid number of 0.05.

5 In another embodiment, the lubricant (C) is a polyoxyalkylene glycol. Useful polyoxyalkylene glycols have a molecular weight between about 300 and about 2000, a viscosity of about 25 to 150 centistokes at 37°C, and a viscosity index of at least 20. The polyoxyalkylene glycols may be polyoxyethylene glycols or polyoxypropylene glycols. Useful polyoxyethylene glycols are available from Union Carbide under the trade name Carbowax PEG 600, 1000 and 1450. The polyoxyalkylene glycols are preferably polyoxypropylene glycols where  
10 the oxypropylene units are at least 80% of the total. The remaining 20% may be ethylene oxide or butylene oxide or other such esters, olefins and the like which may be polarized with polypropylene oxide. Useful polyoxypropylene glycols are available from Union Carbide under the trade names NIAx 425 and NIAx 1025. Useful polyoxypropylene glycols are available from Dow Chemical and sold by the trade names PPG-1200 and PPG-2000.

15 Polyoxyalkylene glycols useful as refrigerator lubricants are described in U.S. Patent 4,755,316 issued to Magid et al. The patent is hereby incorporated by reference for its disclosure to polyoxyalkylene glycols and their use in refrigeration systems.

The polyoxyalkylene glycols may also be capped polyoxyalkylene glycols. Capped polyoxyalkylene glycols generally contain carbyloxy, hydrocarbylcarbyloxy, alkylfluoro, or other capping groups. Capped polyoxyalkylene glycols are described in U.S. Patent 5,152,926 and 4, 971,712.  
20

In another embodiment, the lubricant may be a polycarbonate. Polycarbonate lubricants are prepared by reacting a polyol, monoalcohol, and alkylcarbonate in the presence of a basic catalyst. The polycarbonate lubricants may also be prepared by reacting carbonic diesters, aliphatic dihydric alcohols and phosgene. Examples of carbonic diesters include dimethyl carbonate, diethyl carbonate, and diisobutyl carbonate. Examples  
25 of useful dihydric alcohols include dipropylene glycol, tripropylene glycol, 1,2-butanediol, 1,2-butanediol tetramer, and 2,3-butanediol tetramer. Carbonate lubricants are described in EP 503,410 (Mitsui Petrochemical) and JP 3217495 (Idemitsu Kosan), which are hereby incorporated herein by reference for their disclosure of same.

#### 30 Additive (D)

The liquid compositions may additionally contain (C) at least one additive selected from the group consisting of a phosphorus antiwear agent, a metal deactivator, and mixtures thereof. The phosphorus antiwear agents are present in an amount sufficient to provide antiwear and/or extreme pressure properties to the lubricant and liquid composition. The phosphorus antiwear agents are present in an amount to deliver about  
35 0.001%, or about 0.015%, or about 0.025% to about 1%, or to about 0.5%, or to about 0.2% by weight phosphorus to the lubricant. The phosphorus antiwear agent is generally present in the lubricant in an amount from about 0.01%, or about 0.1% up to about 3%, or to about 2% by weight of the lubricant. The metal deactivator is present in an amount from about 0.001%, or about 0.02%, or about 0.03% up to about 5%, or to about 2%,  
40 or to about 1%, or to about 0.5% by weight of the lubricant.

Examples of phosphorus antiwear include a metal thiophosphate; a phosphoric acid ester or salt thereof; a phosphite; and, a phosphorus-containing carboxylic ester, ether, or amide. The phosphorus acids include the phosphoric, phosphonic, phosphinic, and thiophosphoric acids, including dithiophosphoric acid as well as the monothiophosphoric acid, thiophosphinic, and thiophosphonic acids.

45 In one embodiment, the phosphorus antiwear agent is a phosphorus acid ester prepared by reacting one or more phosphorus acid or anhydride with an alcohol containing from one, or up to about 3, carbon atoms. The alcohol generally contains up to about 30, preferably up to about 24, more preferably up to about 12, carbon atoms. The phosphorus acid or anhydride is generally an inorganic phosphorus reagent, such as phosphorus pentoxide, phosphorus trioxide, phosphorus tetroxide, phosphorus acid, phosphorus halide, lower phosphorus esters, or a phosphorus sulfide and the like. The phosphates may be di- or tri- hydrocarbyl phosphates. Generally the phosphates are di- or tri- alkyl or aryl phosphates. The hydrocarbyl group generally contains from  
50 about 6 to about 24, preferably about 6 to about 18, carbon atoms. When the hydrocarbyl group is an aryl group, then the group contains at least about six carbon atoms. In one embodiment, the phosphate is a di- or tri- aryl phosphate having about six to about eight carbon atoms in each aryl groups. Examples of phosphates include tricresol phosphate (TCP), triphenyl phosphate, trioctyl phosphate, trilauryl phosphate, tristearyl phosphate, trioleyl phosphate, and the like.

55 The phosphite may be a dialkyl or trialkyl phosphite, preferably a dialkyl phosphite. The alkyl phosphonate may be an alkyl phosphonate diester, preferably a dialkylester. The alkyl groups of the phosphite and the phos-

phonate independently contain from 1, or about 3 to about 24, or to about 18, or to about 8 carbon atoms. In one embodiment, the phosphite and the phosphonic acid ester have alkyl groups independently containing from about 3 to about 6, or to about 5, carbon atoms. A number of dialkyl phosphites are commercially available, such as lower dialkyl phosphites, which are preferred. Lower dialkyl phosphites include dimethyl, diethyl, di-  
 5 propyl, dibutyl, dipentyl, and dihexyl phosphites. Phosphites and their preparation are known and many phosphites are available commercially. Also mixed alkyl phosphites, made from a mixture of alcohols, are useful in the present invention. Examples of mixtures of alcohols include ethyl and butyl alcohol, propyl and pentyl alcohol, and methyl and pentyl alcohol. A particularly useful phosphite is dibutyl phosphite.

Alkyl phosphonates are prepared by means known to those in the art. For example, an alkyl phosphonate may be prepared by reacting an alkyl halide with a trialkyl phosphite. Examples of alkyl phosphonates include diethyl, butyl phosphonate; dibutyl, butyl phosphonate; 2-ethylhexyl, 2-ethylhexyl phosphonate; etc.

In another embodiment, the phosphorus antiwear agent is a thiophosphorus ester or salt thereof. The thiophosphorus acid ester may be prepared by reacting a phosphorus sulfide, such as those described above, with an alcohol, such as those described above. The thiophosphorus acid esters may be mono- or dithiophosphorus acid esters. Thiophosphorus acid esters are also referred to generally as thiophosphoric acids.

The phosphorus acid ester may be a monothiophosphoric acid ester or a monothiophosphate. In one embodiment, monothiophosphates are prepared by the reaction of a sulfur source with a dihydrocarbyl phosphite. The sulfur source may for instance be elemental sulfur. The sulfur source may also be a monosulfide, such as a sulfur coupled olefin or a sulfur coupled dithiophosphate. Elemental sulfur is a preferred sulfur source.  
 20 The preparation of monothiophosphates is disclosed in U.S. Patent 4,755,311 and PCT Publication WO 87/07638, which are incorporated herein by reference for their disclosure of monothiophosphates, sulfur sources, and the process for making monothiophosphates. Monothiophosphates may also be formed in the lubricant blend by adding a dihydrocarbyl phosphite to a lubricating composition containing a sulfur source, such as a sulfurized olefin. The phosphite may react with the sulfur source under blending conditions (i.e., temperatures  
 25 from about 30°C. to about 100°C. or higher) to form the monothiophosphate.

In another embodiment, the phosphorus antiwear agent is a dithiophosphoric acid or phosphorodithioic acid. The dithiophosphoric acid may be represented by the formula  $(RO)_2PSSH$  wherein each R is independently a hydrocarbyl group containing from 3 to about 30 carbon atoms. R generally contains up to about 18, or to about 12, or to about 8 carbon atoms. Examples R include isopropyl, isobutyl, n-butyl, sec-butyl, the various amyl, n-hexyl, methylisobutyl carbonyl, heptyl, 2-ethylhexyl, isooctyl, nonyl, behenyl, decyl, dodecyl, and tridecyl groups. Illustrative lower alkylphenyl R groups include butylphenyl, amylphenyl, heptylphenyl, etc. Examples of mixtures of R groups include: 1-butanol and 1-octanol; 1-pentanol and 2-ethyl-1-hexanol; isobutanol and 1-hexanol; isobutyl alcohol and isoamyl alcohol; 2-propanol and 2-methyl-4-pentanol; isopropyl alcohol and sec-butyl alcohol; and isopropyl alcohol and isooctyl alcohol.

In one embodiment, the dithiophosphoric acid may be reacted with an epoxide or a glycol. This reaction product may be used alone, or further reacted with a phosphorus acid, anhydride, or lower ester. The epoxide is generally an aliphatic epoxide or a styrene oxide. Examples of useful epoxides include ethylene oxide, propylene oxide, butene oxide, octene oxide, dodecene oxide, styrene oxide, etc. Propylene oxide is preferred. The glycols may be aliphatic glycols having from 1 to about 12, preferably about 2 to about 6, more preferably  
 40 2 or 3, carbon atoms, or aromatic glycols. Glycols include ethylene glycol, propylene glycol, catechol, resorcinol, and the like. The dithiophosphoric acids, glycols, epoxides, inorganic phosphorus reagents and methods of reacting the same are described in U.S. Patent 3,197,405 and U.S. Patent 3,544,465 which are incorporated herein by reference for their disclosure to these.

Acidic phosphoric acid esters may be reacted with an amine compound or metallic base to form an amine or metal salt. The salts may be formed separately and then the salt of the phosphorus acid ester may be added to the lubricating composition. Alternatively, the salts may also be formed in situ when the acidic phosphorus acid ester is blended with other components to form a fully formulated lubricating composition.

The amine salts of the phosphorus acid esters may be formed from ammonia, or an amine, including monoamines and polyamines. The amines may be primary amines, secondary amines, or tertiary amines. Useful amines include those amines disclosed in U.S. Patent 4,234,435 at Col. 21, line 4 to Col. 27, line 50, these passages being incorporated herein by reference. Any of the above described amines or amides may form the salts.

In one embodiment, the phosphorus antiwear agent is a metal thiophosphate, preferably a metal dithiophosphate. The metal thiophosphate is prepared by means known to those in the art. Examples of metal dithiophosphates include zinc isopropyl, methyl amyl dithiophosphate, zinc isopropyl isooctyl dithiophosphate, barium di(nonyl)-dithiophosphate, zinc di(cyclohexyl) dithiophosphate, zinc di(isobutyl) dithiophosphate, calcium di(hexyl) dithiophosphate, zinc isobutyl isoamyl dithiophosphate, and zinc isopropyl secondary-butyl dithiophosphate.



In another embodiment, the phosphorus antiwear agent is a metal salt of (a) at least one dithiophosphoric acid and (b) at least one aliphatic or alicyclic carboxylic acid. The dithiophosphoric acids are described above. The carboxylic acid may be a monocarboxylic or polycarboxylic acid, usually containing from 1 to about 3, or just one carboxylic acid group. The preferred carboxylic acids are those having the formula  $R^{\#}COOH$ , wherein  
 5  $R^{\#}$  is an aliphatic or alicyclic hydrocarbyl group preferably free from acetylenic unsaturation.  $R^{\#}$  generally contains from about 2, or from about 4 carbon atoms.  $R^{\#}$  generally contains up to about 40, or up to about 24, or to up about 12 carbon atoms. In one embodiment,  $R^{\#}$  contains from 4, or from about 6 up to about 12, or up to about 8 carbon atoms. In one embodiment,  $R^{\#}$  is an alkyl group. Suitable acids include the butanoic, pentanoic, hexanoic, octanoic, nonanoic, decanoic, dodecanoic, octodecanoic, and eicosanoic acids, as well as  
 10 olefinic acids such as oleic, linoleic, and linolenic acids and linoleic acid dimer. A preferred carboxylic acid is 2-ethylhexanoic acid. U.S. Patents 4,308,154 and 4,417,990 describe procedures for preparing these metal salts and disclose a number of examples of such metal salts. These patents are hereby incorporated by reference for those disclosures.

In one embodiment, the phosphorus antiwear agent is a phosphorus containing amide. The phosphorus  
 15 containing amides are prepared by the reaction of one of the above described phosphorus acids, preferably a dithiophosphoric acid, with an unsaturated amide. Examples of unsaturated amides include acrylamide, N,N'-methylene bisacrylamide, methacrylamide, crotonamide, and the like. The reaction product of the phosphorus acid and the unsaturated amide may be further reacted with a linking or a coupling compound, such as formaldehyde or paraformaldehyde. The phosphorus-containing amides are known in the art and are disclosed  
 20 in U.S. Patents 4,670,169, 4,770,807, and 4,876,374 which are incorporated by reference for their disclosures of phosphorus amides and their preparation.

In one embodiment, the phosphorus antiwear agent is a phosphorus containing carboxylic ester. The phosphorus containing carboxylic esters are prepared by reaction of one of the above-described phosphorus acids, preferably a dithiophosphoric acid, and an unsaturated carboxylic acid or ester. If the carboxylic acid is used,  
 25 the ester may then be formed by subsequent reaction of the phosphoric acid-unsaturated carboxylic acid adduct with an alcohol, such as those described herein. In one embodiment, the alcohol has from 1 to about 12 carbon atoms.

In one embodiment, the unsaturated carboxylic ester is a vinyl ester. The vinyl ester may be represented by the formula  $R^{\#}_1CH=CH-O(O)CR^{\#}_2$ , wherein  $R^{\#}_1$  is a hydrocarbyl group having from 1 to about 30, or to about  
 30 12 carbon atoms, preferably hydrogen, and  $R^{\#}_2$  is a hydrocarbyl group having 1 to about 30, or to about 12, or to about 8 carbon atoms. Examples of vinyl esters include vinyl acetate, vinyl 2-ethylhexanoate, vinyl butanoate, etc.

In one embodiment, the unsaturated carboxylic acid or ester includes maleic, fumaric, acrylic, methacrylic, itaconic, citraconic acids and esters. The ester may be represented by one of the formulae;  
 35  $R^*C=C(R^*_1)C(O)OR^*_2$ , or  $R^*_2O-(O)C-HC=CH-C(O)OR^*_2$ , wherein each  $R^*$  and  $R^*_2$  are independently hydrogen or a hydrocarbyl group having 1 to about 18, or to about 12, or to about 8, carbon atoms, and  $R^*_1$  is hydrogen or an alkyl group having from 1 to about 6 carbon atoms. In one embodiment,  $R^*_1$  is preferably hydrogen or a methyl group.

Examples of unsaturated carboxylic esters include methyl acrylate, ethyl acrylate, 2-ethylhexyl acrylate,  
 40 2-hydroxyethyl acrylate, ethyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 2-hydroxypropyl acrylate, ethyl maleate, butyl maleate, and 2-ethylhexyl maleate. The above list includes mono- as well as diesters of maleic, fumaric, and citraconic acids.

In one embodiment, the phosphorus antiwear agent is a reaction product of a phosphorus acid, preferably a dithiophosphoric acid, and a vinyl ether. The vinyl ether is represented by the formula  $R^*_3-CH_2=CH-OR^*_4$ ,  
 45 wherein  $R^*_3$  is independently hydrogen or a hydrocarbyl group having 1 to about 30, preferably to about 24, more preferably to about 12, carbon atoms.  $R^*_4$  is a hydrocarbyl group defined the same as  $R^*_3$ . Examples of vinyl ethers include vinyl methylether, vinyl propylether, vinyl 2-ethylhexylether, and the like.

The lubricant may additionally contain a metal deactivating agent. Useful metal deactivating agents include nitrogen-containing heterocycles, such as dimercaptiothiadiazoles, triazoles, amino-mercaptiothiadiazoles,  
 50 imidazoles, thiazoles, tetrazoles, hydroxyquinolines, oxazolines, imidazolines, thiophenes, indoles, indazoles, quinolines, benzoxazines, dithiols, oxazoles, oxatriazoles, pyridines, piperazines, triazines, and derivatives of any one or more thereof.

In one embodiment, the nitrogen containing heterocycle is a triazole or derivative thereof, a thiazole or derivative thereof, a mercaptothiazole or derivative thereof, and a thiadiazole or derivative thereof, preferably  
 55 a triazole or derivative thereof. These additives provide metal deactivating, metal passivating, and corrosion controlling character to the liquid compositions. Examples of useful metal deactivators include dimercaptiothiadiazoles and derivatives thereof, substituted and unsubstituted triazoles (e.g., benzotriazole, tolyltriazole, octylbenzotriazole, and the like), mercaptobenzothiazoles, etc. Examples of these compounds are benzotriazole,

alkyl-substituted benzotriazole (e.g., tolyltriazole, ethylbenzotriazole, hexylbenzotriazole, octylbenzotriazole, etc.), aryl-substituted benzotriazole (e.g., phenol benzotriazoles, etc.), and alkylaryl- or arylalkyl-substituted benzotriazole and substituted benzotriazoles where the substituent may be hydroxy, alkoxy, halo (especially chloro), nitro, carboxy, and carboxyalkoxy. Preferably, the triazole is a benzotriazole or an alkylbenzotriazole in which the alkyl group contains 1 to about 20 carbon atoms, preferably 1 to about 8 carbon atoms.

The nitrogen containing heterocycle (C) may also be the reaction product of at least one of the above triazoles, at least one amine and an aldehyde or aldehyde precursor. The triazole is preferably a benzotriazole. The amine can be one or more mono- or polyamines. These monoamines and polyamines can be primary amines, secondary amines, or tertiary amines. Examples of polyamines include polyalkylenepolyamines and heterocyclic polyamines. The polyalkyleneamines include polyethylenepolyamines, such as diethylenetriamine, triethylenetriamine, tetraethylenepentaamine, etc.

The aldehyde is typically a hydrocarbon-based aldehyde, preferably a lower aliphatic aldehyde. Suitable aldehydes include formaldehyde, benzaldehyde, acetaldehyde, the butyraldehydes, hydroxybutyraldehydes, and heptanals, as well as aldehyde precursors which react as aldehydes under the conditions of the reaction such as paraformaldehyde, paraldehyde, formalin, trioxane, and methanal. Formaldehyde and its precursors (e.g., paraformaldehyde, trioxane) are preferred. Mixtures of aldehydes may be used.

An example of a useful triazole derivative is Reomet® 39. This material is a triazole derivative available commercially from Ciba-Geigy Corporation.

Other additives may be included in the liquid compositions of the present invention to enhance the performance of the liquids include extreme-pressure and anti-wear agents, oxidation and thermal-stability improvers, corrosion-inhibitors, viscosity-index improvers, pour point and/or floc point depressants, dispersants, anti-foaming agents, viscosity adjusters, metal deactivators, acid acceptors, etc. As noted above, these supplementary additives should not substantially impair the overall performance of the liquid compositions of the invention. Included among the materials which may be used as extreme-pressure and antiwear agents are chlorinated waxes; sulfurized fats and olefins; such as soybean oil, and olefins having from about three to about 12 carbon atoms; fatty acids, such as oleic acid; molybdenum complexes; borates, including borated fatty epoxides, borated amines, and borate esters having from about four to about 24 carbon atoms in each ester group; sulfurized Diels Alder adducts; organic sulfides, including dibenzyl disulfide and dibutyl tetrasulfide; metal salts of organic acids, including zinc oleate; metal thiocarbamates, such as zinc dioctyldithiocarbamate and barium diheptylphenyl dithiocarbamate; amine dithiocarbamates; dithiocarbamate esters, such as reaction products of an amine, (e.g., butylamine), carbon disulfide and unsaturated compounds selected from acrylic, methacrylic, maleic, or fumaric acids, esters, or salts and acrylamides; and alkylene- or sulfur-coupled dithiocarbamate such as methylene or phenylene coupled bis(dibutyldithiocarbamates); etc. Sterically hindered phenols, aromatic amines, dithiophosphates, sulfides, and metal salts of dithioacids are useful examples of oxidation and thermal stability improvers. Compounds useful as corrosion-inhibitors include organic acids, organic amines, organic alcohols, metal sulfonates, etc. VI improvers include polyolefins such as polyester, polybutene, polymethacrylate, polyalkyl styrenes, etc. Pour point and floc point depressants include polymethacrylates, ethylene-vinyl acetate copolymers, succinamic acid-olefin copolymers, ethylene-alpha olefin copolymers, etc. Silicone polymers are a well known type of anti-foam agent. Viscosity adjusters are exemplified by polyisobutylene, polymethacrylates, polyalkyl styrenes, naphthenic oils, alkyl benzene oils, polyesters, polyvinyl chloride, polyphosphates, etc. Acid acceptors include epoxides and epoxidized oils, such as soybean oil.

The liquid compositions of the present invention are particularly useful as refrigerants in various refrigeration systems which are compression-type systems such as refrigerators, freezers, and air-conditioners including automotive, home and industrial air-conditioners. The following examples are illustrative of the liquid compositions of the present invention.

		<u>Parts by Wt.</u>
50	<u>Example A</u>	
	HFC-134a	90
	Lubricant of Example 7	9.5
55	Ethomeen O/12 <sup>1</sup>	0.5

Example B

	1,1,1,2-tetrafluoroethane	85
5	Lubricant of Example 11	13.9
	Ethomeen O/12	0.5
	DBPH	0.6

Example C

	HFC-134a	55
	Lubricant of Example 13	44.7
15	Ethomid O/15	0.3

Example D

	HFC-134a	60
20	Product of Example 16	39.59
	Ethomid O/15	0.3
	Dibutyl phosphite	0.1
25	benzotriazole	0.01

Example E

	HFC-134a	85
30	Product of Example 18	14.48
	Ethomeen O/12	0.5
35	Reomet® 39	0.02

The following examples relate to tests performed on the liquid compositions of the present invention. The Falex wear tester measures the load carrying ability of lubricants. The test consists of a rotating test pin between loaded V-blocks. The rotating pin and block are immersed in the test lubricant, and the blocks are loaded at 300 pounds for five hours. The test pin is AISI 3135 steel, and the V-blocks are 390 aluminum. The test is run in the presence of HFC-134a. The test measures notch wear of the block and the weight change of the pin and block.

Test fluid A is an ester fluid having a kinematic viscosity of 32 cSt at 40°C. The ester is prepared by blending 30% by weight of a triester of trimethylolpropane and n-pentanoic acid, having a kinematic viscosity of 10 cSt at 40°C, and 70% by weight of an ester prepared by reacting n-pentanoic acid, iso-octanoic acid, and 3,5,5-trimethylhexanoic acid with monopentaerythritol, wherein the weight ratio of the acids is (15:30:55), and wherein the product has a kinematic viscosity at 40°C of 68 cSt. Test fluid B contains the ester of test fluid A plus 0.62% by weight dibutyl phosphite and 0.01% tolyltriazole. Test fluid C is the same as test fluid B plus 0.25% by weight of Ethomeen O/12.

Falex Tests

5	Test Fluid	HFC-134a (psig)	Notch Wear (mm)	Pin Weight Change (mg)
10	A	40	0.241	-119.9
	B	40	0.060	-24.5
15	C†	40	0.023	-0.6
	A	5-10	0.145	-47.3
	B	5-10	0.038	-6.6
20	C†	5-10	0.028	-0.6

† gave only a trace of visible metal debris.

As can be seen from the above data, the test fluids containing the fatty amine have improved wear characteristics, such as reducing notch wear and pin weight loss.

In addition improved aluminum wear is shown by a reduction in the scar width on the aluminum block. The test fluids give scar width shown as follows.

Fluid A 1.2 mm

Fluid B 0.8 mm

Fluid C 0.6 mm

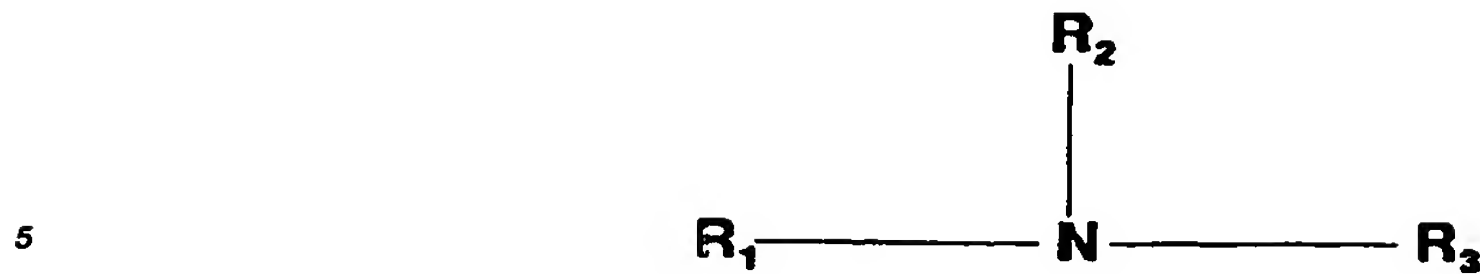
Lower scar widths reflect reduced aluminum wear.

While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

Claims

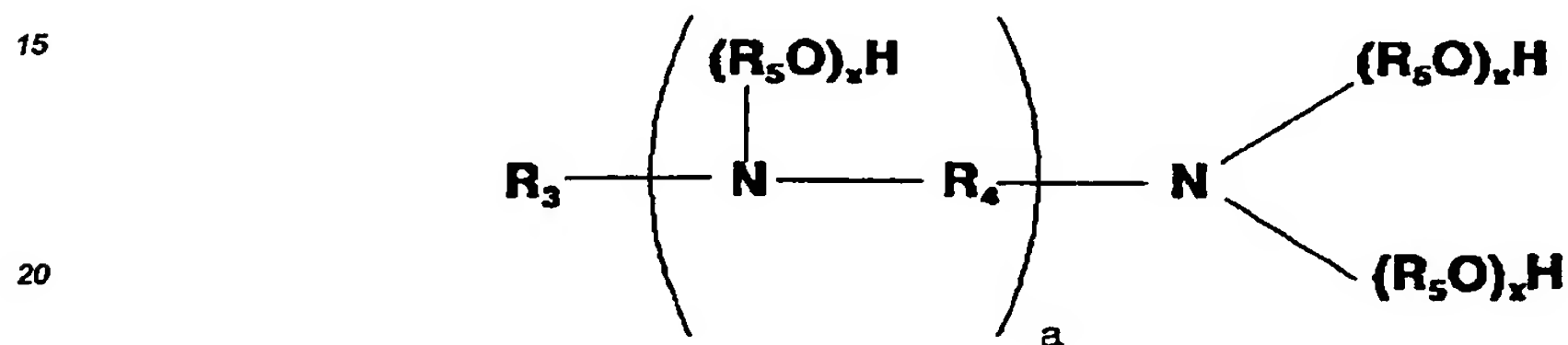
1. A liquid composition comprising (A) at least one fluorine-containing hydrocarbon containing 1 to 3 carbon atoms, (B) an efficiency improving or wear reducing amount of an additive selected from at least one fatty amine, at least one fatty amide, at least one reaction product of at least one fatty carboxylic acylating agent and at least one amine selected from a polyamine, a hydroxy amine and a mixture thereof, and at least one mixture thereof, and (C) an effective amount of a lubricant selected from at least one carboxylic ester, at least one polyalkylene glycol, at least one polycarbonate, and at least one mixture thereof.
2. A liquid composition of claim 1 wherein fluorine is the only halogen in the fluorine-containing hydrocarbon.
3. A liquid composition of either of claims 1 and 2 wherein said fatty amine is represented by the formula:





10 where  $\text{R}_1$  is a hydrocarbyl group containing from about 8 to about 30 carbon atoms, and  $\text{R}_2$  and  $\text{R}_3$  are each independently hydrogen, an alkyl group containing from one to about twenty carbon atoms, a hydroxyalkyl group, a carboxy, a hydrocarbylcarboxy, or a polyoxyalkylene group.

4. A liquid composition of any preceding claim wherein said additive is represented by the formula



25 wherein  $\text{R}_3$  is a hydrocarbyl group containing from about 8 to about 30 carbon atoms,  $\text{R}_4$  and  $\text{R}_5$  are each independently an alkylene group,  $a$  is zero or one, and each  $x$  is independently a number from zero to about 25, with the proviso that at least one of  $x$  is at least one.

- 30 5. A liquid composition of claim 4 wherein  $\text{R}_3$  is an octyl, decyl, decenyl, dodecyl, dodecenyl, tridecyl, tetradecyl, hydroxytetradecyl, hexadecyl, hydroxyhexadecyl, octadecyl, oleyl, coco, soya or tallow group, each  $\text{R}_5$  independently contains from about two to about six carbon atoms,  $a$  is zero, and each  $x$  is independently a number from one to about five.

6. A liquid composition of any preceding claim wherein said additive is represented by the formula:



40 wherein  $\text{R}_7$  is a hydrocarbyl group containing from about 8 to about 30 carbon atoms, and each  $\text{R}_8$  is independently hydrogen, a hydrocarbyl group containing from one to about twenty carbon atoms, a hydroxyalkyl group, or a polyoxyalkylene group.

- 45 7. A liquid composition of any preceding claim wherein said additive is a polyoxyalkylated oleylamide, stearylamide, tallowamide, soyamide, cocoamide, or laurylamide.
8. A liquid composition of any preceding claim wherein said carboxylic ester is a carboxylic ester of a polyhydroxy compound containing at least 2 hydroxy groups and characterized by the general formula



wherein  $\text{R}_9$  is a hydrocarbyl group, each  $\text{R}_{10}$  is independently hydrogen, a straight chain lower hydrocarbyl group, a branched chain hydrocarbyl group, or a straight chain hydrocarbyl group containing from 8 to

about 22 carbon atoms provided that at least one R<sup>10</sup> group is hydrogen, a lower straight chain hydrocarbyl or a branched chain hydrocarbyl group, or a carboxylic acid- or carboxylic acid ester-containing hydrocarbyl group, and n is at least 2.

- 5 9. A liquid composition of any preceding claim wherein said carboxylic ester is at least one carboxylic ester of at least one polyhydroxy compound and a member selected from:  
    (a) at least one monocarboxylic acylating agent having from about 4 to about 15 carbon atoms,  
    (b) at least one branched chain monocarboxylic acylating agent having from about 8 to about 9 carbon atoms,  
10 (c) at least one straight chain monocarboxylic acylating having from about 4 to about 6 carbon atoms,  
    (d) at least one mixture of  
        (i) at least one monocarboxylic acylating agent having from about four to about five carbon atoms and  
        (ii) (b) at least one monocarboxylic acylating agent having from about 7 to about 15 carbon atoms, and  
15 (e) combinations thereof.
10. A liquid composition of any preceding claim wherein said carboxylic ester is at least one carboxylic ester of a polyhydroxy compound and at least one combination of (i) at least one polycarboxylic acylating agent and (ii) at least one monocarboxylic acylating agent having from about 4 to about 15 carbon atoms.  
20
11. A liquid composition of claim 10 wherein said monocarboxylic acylating agent (i) is at least one branched chain monocarboxylic acylating agent having from about 8 to about 9 carbon atoms, and said polycarboxylic acylating agent (ii) contains from about 2 to about 12 carbon atoms.
- 25 12. A liquid composition of any one of claims 9 to 11 wherein said polyhydroxy compound is selected from neopentyl glycol, glycerol, trimethylolpropane, di(trimethylolpropane), pentaerythritol, dipentaerythritol, tripentaerythritol, and mixtures thereof.
- 30 13. A liquid composition of any preceding claim further comprising (D) at least one member selected from at least one phosphorus antiwear agent, at least one metal deactivator, and a mixture thereof.
14. A liquid composition of claim 13 wherein said phosphorus antiwear agent is selected from at least one alkyl or aryl phosphite, at least one alkyl phosphonate ester, at least one alkyl or aryl phosphate, at least one phosphorus containing ester, amide or ether, and at least one mixture thereof.  
35
15. A liquid composition of either of claims 13 and 14 wherein said member (D) is selected from at least one aryl phosphate having from about 6 to about 12 carbon atoms, at least one alkyl phosphite independently having from about one to about 20 carbon atoms in each alkyl group, and at least one alkyl phosphonate independently having from about one to about 20 carbon atoms.  
40
16. A liquid composition of any one of claims 13 to 15 wherein said member (D) is at least one nitrogen-containing heterocycle.
17. A liquid composition of claim 16 wherein said nitrogen-containing heterocycle is at least one triazole or derivative thereof.  
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18. A liquid composition of claim 16 wherein said nitrogen-containing heterocycle is tolyltriazole, benzotriazole, or at least one reaction product of at least one benzotriazole, at least one amine, and at least one aldehyde or aldehyde precursor.
- 50 19. A liquid composition of any one of claims 13 to 18 wherein said member (D) is a mixture of at least one alkyl phosphite independently having from about 1 to about 20 carbon atoms in each alkyl group, and at least one triazole or derivative thereof.
20. A liquid composition of any one of claims 13 to 19 wherein said member (D) is tricresylphosphate, dibutyl phosphite, or dibutyl butyl phosphonate.  
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21. A composition comprising (B) at least one fatty amine and (C) at least one carboxylic ester or at least one polyalkylene glycol lubricant.

22. A method of lubricating a compressor comprising the steps of introducing to said compressor (A) at least one fluorine-containing hydrocarbon containing 1 to 3 carbon atoms, (B) an efficiency improving or wear reducing amount of an additive selected from at least one fatty amine, at least one fatty amide, and at least one mixture thereof, and (C) an effective amount of a lubricant selected from at least one carboxylic ester, at least one polyalkylene glycol, at least one polycarbonate, and at least one mixture thereof, and operating the compressor.

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European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 94 30 1146

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
X	EP-A-0 523 561 (IDEMITSU KOSAN COMPANY LIMITED)  * page 3, line 30 - line 42 * * page 3, line 51 - line 53 * * page 4, line 20 - line 23 * * page 4, line 40 - line 44 * * page 5, line 12 *	1-3, 8, 9, 12-15, 21, 22	C10M169/04 C10M171/00 //(C10M169/04, 105:38, 105:40, 105:42, 105:48, 107:32, 107:34, 133:06, 133:08, 133:16, 133:44, 137:02, 137:04, 137:12, 149:12), C10N40:30
P, X	EP-A-0 538 478 (SANYO ELECTRIC)  * page 3, line 3 - line 4 * * page 4, line 24 * * page 4, line 27 - line 28 *	1-3, 13-15, 20-22	
X	& WO-A-92 19704 (SANYO ELECTRIC) 12 November 1992	1-3, 13-15, 20-22	
X	WO-A-93 01249 (THE LUBRIZOL CORPORATION)  * page 23; example 21 * * page 29; examples IX, X * * claim 10 *	1, 2, 6, 10-22	TECHNICAL FIELDS SEARCHED (Int. CL.5)  C10M C09K
A	WO-A-91 15552 (THE LUBRIZOL CORPORATION) * claims 1, 5, 9 *	6, 7	
A	US-A-4 231 883 (R.E. MALEC) * column 1, line 30 - line 45 * * column 2, line 33 - line 34 * * column 3, line 7 - line 8 *	4, 5	
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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 29 April 1994	Examiner Hilgenga, K
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document</p>			

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# EUROPEAN SEARCH REPORT

Application Number  
EP 94 30 1146

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
A	WO-A-90 05174 (THE LUBRIZOL CORPORATION) * page 16; example 6 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. CL.5)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 29 April 1994	Examiner Hilgenga, K
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons</p> <p>-----  &amp; : member of the same patent family, corresponding document</p>			

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